

Polymeric alkali fullerides are stable in air

Daniel Koller, Michael C. Martin, Peter W. Stephens, and Laszlo Mihaly^{a)}
Department of Physics, State University of New York at Stony Brook, New York 11794-3800

Sandor Pekker
Research Institute for Solid State Physics, POB 49, H-1525 Budapest, Hungary

Andras Janossy
Institute of Physics, Technical University of Budapest, H-1521, Budapest, Hungary

Olivier Chauvet and Laszlo Forro
Laboratoire de Physique des Solides Semicrystallines, IGA, Department of Physics, EPFL, 1015 Lausanne, Switzerland

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Infrared transmission, electron spin resonance, and x-ray diffraction measurements show unambiguously that RbC_{60} and KC_{60} are stable in air, in contrast to Rb_6C_{60} which decomposes rapidly upon exposure. The specimens studied transform to pure C_{60} and other by-products when heated above 100 °C, approximately the temperature of the orthorhombic-fcc phase transition. The stability of these compounds raises the possibility of applying them as protective layers for the superconducting fullerides. © 1995 American Institute of Physics.

The compounds of alkali metals (A) with fullerenes (C_{60}) are the subject of considerable recent interest. Superconductivity was discovered in A_3C_{60} ,^{1,2} and a polymeric chain structure^{3,4} with metallic properties^{5,6} was seen in A_1C_{60} . Other fullerides of composition A_4C_{60} and A_6C_{60} have also been studied.² Early investigations established that some of these materials rapidly decompose if exposed to air, and extreme care has been taken to treat all samples in an inert atmosphere.² Yet here we report infrared (IR) spectroscopy, electrons in response (ESR), and x-ray diffraction experiments, indicating that two fullerides, RbC_{60} and KC_{60} are stable in air.

The A_1C_{60} compounds have a fcc (rocksalt) structure at high temperature,⁷ and upon slow cooling they undergo a reversible first-order phase transition to an orthorhombic state, where the C_{60} molecules are chemically bonded to form linear chains.^{3,4} This “polymeric” state is thermodynamically stable at room temperature for RbC_{60} . Phase separation of KC_{60} to K_3C_{60} and pure C_{60} was reported by several authors.⁷⁻⁹ However, for the slowly cooled samples in this study we consistently found large amounts of polymeric phase of both RbC_{60} and KC_{60} by ESR, x-ray diffraction,⁴ and IR spectroscopy. Further investigations are clearly needed in this respect, but the basic conclusions of the present work are not expected to change.

In the present study three separately prepared sets of samples were investigated. RbC_{60} thin films (specimen S1) were made on Si substrates under vacuum in a special sample cell.¹⁰ Doping was performed by exposing the films to Rb vapor. During doping the temperature of the film was 225 °C and the composition was monitored *in situ* by recording IR spectra, and following the evolution of the $\text{F}_{1u}(4)$ molecular vibration.^{9,11} Polycrystalline KC_{60} (specimen S2) was made by coevaporation of stoichiometric amounts of the constituent materials in a sealed tube, placed in a gradient

furnace.¹² Crystals of typical size ~ 0.1 mm grew at a temperature of about 300 °C, while the C_{60} and K were kept at 600 and 150 °C, respectively. During the course of the experiments samples S1 and S2 were first investigated under vacuum or inert atmosphere, and were later exposed to air. A part of the pristine S2 sample was further processed to produce iodine treated KC_{60} . The iodination was carried out in a glove box by immersing the coevaporation crystals to a dilute solution of iodine in toluene for four days. The mixture was then repeatedly rinsed with toluene, ethanol, and pentane in air. Specimen S3 was the insoluble residue, left behind after this process. This sample was stored in air for about a month before the measurements reported here were completed.

IR transmission measurements were carried out on samples S1 and S3. First the spectrum of the pristine sample S1 was recorded. The low overall transmission and the characteristic resonance structure^{6,13} of RbC_{60} were clearly visible (lower curve of Fig. 1). The IR spectrum indicates that S1 also contains measurable amounts of Rb_6C_{60} and pure C_{60} . Then the hermetically sealed sample cell was opened to air. The spectrum taken immediately afterwards (~ 10 min) shows the same RbC_{60} resonance lines, slightly increased transmission, and the absence of the Rb_6C_{60} impurity phase (Fig. 1, upper curve). Therefore we conclude that Rb_6C_{60} was destroyed and RbC_{60} is stable. The small increase in overall transmission is most likely due to the removal of a small amount of metallic Rb_3C_{60} from the pristine sample. The corresponding Rb_3C_{60} resonance line, positioned at 1364 cm, is expected to be below the noise level of the experiment. Pure C_{60} , most likely produced in the chemical reactions after air exposure, has a much weaker IR signal than Rb_6C_{60} or Rb_3C_{60} ^{9,11,14} and does not change the magnitude of the existing C_{60} signal by any appreciable amount.

The IR spectrum of the iodine treated sample S3 is also dominated by the polymeric KC_{60} signal (Fig. 2). This specimen was used to demonstrate that the compound is unstable

^{a)}Electronic mail: lmihaly@ccmail.sunysb.edu

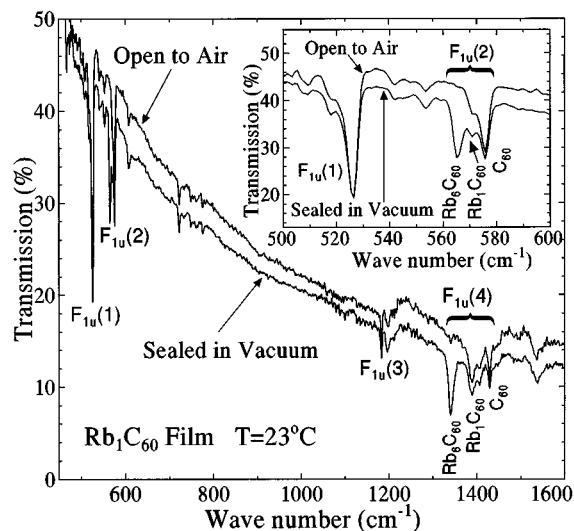


FIG. 1. IR transmission spectra of a thin Rb-doped C_{60} film (specimen S1). Inset shows the lower two vibrational modes on an expanded scale. The sample was cooled at a rate of $\sim 10^\circ\text{C}/\text{min}$ to room temperature from the preparation temperature. The first specimen (lower curve) was measured on the pristine film in vacuum. The lines at 1387 and 1406 cm^{-1} derive from the $F_{1u}(4)$ molecular vibration, split by the polymerization. The $F_{1u}(2)$ and $F_{1u}(4)$ derived resonances corresponding the Rb_6C_{60} are also clearly visible. When the sample is exposed to air (upper curve), the Rb_6C_{60} is destroyed, while the RbC_{60} remains.

if moderately heated. Upon heating the transmission increased dramatically, the split $F_{1u}(4)$ line of RbC_{60} at 1387 and 1406 cm^{-1} disappeared and a strong C_{60} line appeared; i.e., the sample transformed into a mixture consisting of pure C_{60} and other compounds with no strong IR resonances in the measured frequency range. The decomposition starts very slowly below 100°C , but it is complete at $T=200^\circ\text{C}$. The sample was heated in several steps in the IR spectrometer,

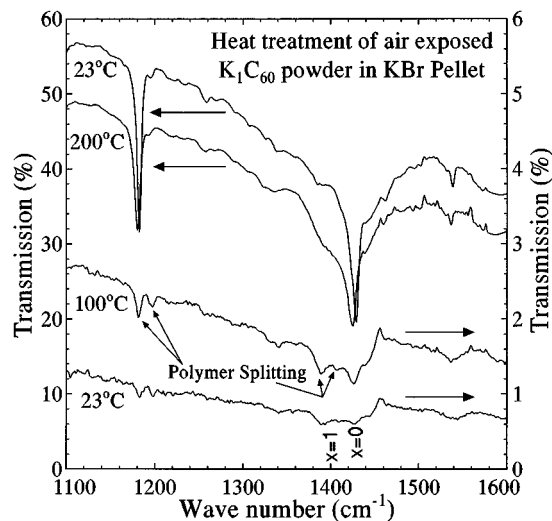


FIG. 2. IR transmission of the iodine treated KC_{60} powder (specimen S3) in a KBr pellet. The spectral features before heating indicate that the majority of the sample is KC_{60} . Upon heating, the sample decomposes. The right-hand side scale, which belongs to the lower two curves, is expanded by a factor of 10 relative to the left-hand side scale.

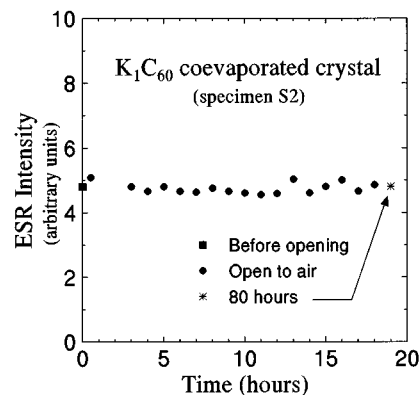


FIG. 3. Time dependence of the ESR intensity of a polycrystalline KC_{60} sample (specimen S2) after exposure to air.

and it reached 200°C in about 3 h. As illustrated by the uppermost spectrum at room temperature, the decomposition is irreversible.

The coevaporation crystals (S2), as well as S3, were used in the ESR measurements. KC_{60} and RbC_{60} have a characteristically narrow ESR line.^{5,15} The ESR spectrum of sample S1 was recorded at room temperature, with the sample sealed in a quartz tube. The tube was then opened to air, and the ESR signal was measured for several days. Figure 3 shows that the signal intensity (a) did not change after opening the sample to air and (b) was independent of time within the accuracy of the measurement. The width of the signal was also unchanged. We emphasize that the most likely by-products of the disintegration of KC_{60} (C_{60} and K_2O or KOH) have no ESR signal. If free radicals or other paramagnetic materials are produced, then it is extremely unlikely that their signals mimic the KC_{60} signal so accurately. The ESR signal of sample S3 is also characteristic of polymeric KC_{60} , and the magnetic susceptibility remains constant down to 50 K , indicating the metallic nature of electrons, similar to pristine polymeric KC_{60} .⁵

X-ray spectroscopy was also performed on the iodine treated sample, S3. The diffraction spectrum (Fig. 4) shows an enhanced background, possibly due to a noncrystalline component, but the majority of the crystalline part is clearly orthorhombic KC_{60} .⁴ All three of the probes, x-ray, ESR, and IR spectroscopy, sensitive to various physical properties of the sample, show that the air-exposed specimens are mostly polymeric A_1C_{60} .

The experimental data presently available to us is not sufficient to completely explain the unexpected stability of polymeric alkali metal fullerenes. Some C_{60} salts with a C^- anion, like the (TDAE) C_{60} or the chromium (III) porphyrin salt, were found to be sensitive to air,^{16,17} while others, like (tetraphenyl phosphonium) C_{60} , are stable.¹⁷ In principle, stability is observed if the material is in a thermodynamically favored configuration (like gold in air) or it may be covered by a protecting layer (like aluminum in air). The linear chain structure⁴ and morphology¹² of the AC_{60} compounds suggest a more exotic possibility: the long C_{60} polymer chains inhibit the diffusion of the alkali metal or the oxygen, effec-

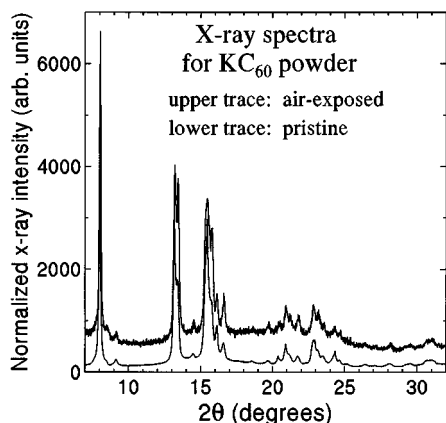


FIG. 4. X-ray diffractogram of the iodine exposed KC_{60} (specimen S3), as compared to a pristine polycrystalline sample, used in the detailed Rietveld analysis of the polymeric structure (Ref. 4).

tively leading to a much slower one-dimensional diffusion, and hence a greatly enhanced lifetime.

The existence of a stable alkali metal fulleride may have far-reaching consequences for the study and application of fullerides. Sample preparation procedures and measurements are much simpler if the specimens can be freely moved and exchanged in air. Investigation of the dc electrical properties will clarify if intergrain potential barriers are present, possibly inhibiting the electronic transport. In any case, thermal, magnetic, and optical studies are greatly simplified. The stable RbC_{60} or KC_{60} polymer may have applications as a protective skin for the superconducting K_3C_{60} or Rb_3C_{60} material. In fact, the present results may shed some light on early reports of unexpected persistence of the superconducting Meissner signal in some air exposed A_3C_{60} samples.¹⁸ We hypothesize that a fraction of the material in those samples was doped incompletely, leading to the formation of A_1C_{60} , which then encapsulated the A_3C_{60} .

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